CONF-941013--28

Formation of Anisotropic Tl-1212, Tl-2212, Tl-1223 and Tl-2223 Particles using Aerosol Flow Reacted Powders

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Abstract — Highly anisotropic particles of Tl-1212, Tl-2212, Tl-1223 and Tl-2223 superconductors were grown. The Tl-free precursor powders with the compositions $Ba_1Ca_2Cu_3Ag_{0.37}O_6$ and $Ba_2Ca_2Cu_3Ag_{0.37}O_7$ were prepared using an aerosol flow reactor. These precursor powders were then post-annealed in 0.1 atm oxygen at 700 °C for 4h to reduce the carbon present and mixed with Tl_2O_3 (typical composition of Tl_x; x = 0.6-1.0). The Tl-containing powders were heated in sealed gold tubes between 650-890 °C for various times. X-ray diffraction showed that the Tl-2212 and Tl-2223 phases were stable over a wide range of temperatures. Scanning electron microscopy showed evidence for the presence of high aspect-ratio particles. These highly anisotropic particles may of interest for the preparation of powder-in-tube and other powder deposited conductors, for current leads, and for grain alignment studies.

I. INTRODUCTION

The observation of high critical currents and good "in-field" transport property measurements at temperatures > 40 K in $TlBa_2Ca_2Cu_3O_9$ or $(Tl,Pb)(Sr,Ba)_2Ca_2Cu_3O_9$ (both referred to as Tl-1223) superconductors give these materials great technological importance for 40 K applications [1]-[4]. For the fabrication of superconducting wires, tapes, powder-deposited conductors and magnetic shields, fine homogeneous precursor powders are necessary. A promising method for producing superconducting powders is the gas-phase decomposition of aerosol droplets containing inorganic precursors [5]. The aerosol pyrolysis technique can produce high quality powders with reproducible phase content, particle morphology, size distribution and microstructure, but synthesis of complex oxide aerosol precursor powders and their subsequent thallination require studies of grain growth, chemical reactions and phase transitions during processing. In this work, we report the formation of submicron size particles of precursor powders by aerosol decomposition of the starting nominal compositions $Ba_2Ca_2Cu_3Ag_{0.37}O_7$ and $Ba_1Ca_2Cu_3Ag_{0.37}O_6$. These precursor powders were then mixed stoichiometrically with Tl_2O_3, and heat-treated at various temperatures and different periods of times in sealed gold tubes. Highly anisotropic particles of Tl-2212, Tl-2223, Tl-1212 and Tl-1223 superconductors were obtained at different temperatures.

Manuscript received October 17, 1994.

This work was sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, US Department of Energy and technology development was funded by the US Department of Energy Office of Advanced Utility Concept-Superconductor Technology Program, both under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. This work was also supported by the Oak Ridge National Laboratory Postdoctoral Research Program, administered jointly by the ORISE and ORNL.

II. EXPERIMENTAL ASPECTS

Precursor powders with the nominal compositions $Ba_2Ca_2Cu_3Ag_{0.37}O_7$ and $Ba_1Ca_2Cu_3Ag_{0.37}O_6$ were prepared by aerosol decomposition. An aqueous solution of Ba, Ca, Cu and Ag nitrates with stoichiometry Ba:Ca:Cu:Ag = 2(or1):2:3:0.37 (5 weight % Ag in fully reacted powder) and a Cu^{2+} concentration of 0.1 M was prepared by dissolving $BaCO_3$, $CaCO_3$, CuO and $AgNO_3$ in HNO_3. The pH of the solution was approximately 1. An aerosol was generated from the precursor solution using a commercial atomizer and was carried through an alumina reactor tube which is kept inside a tube furnace. The furnace was maintained at a temperature of 850 °C, and the flow was adjusted to obtain residence times of 1-25 sec within the decomposition zone, and the oxide powders were collected on a silver membrane filter. Argon-oxygen (2 %) gas was used the carrier gas. A schematic diagram of the powder generation apparatus is shown in Figure 1. Pyrolysis temperature, residence time and carrier gas compositions were the key process parameters for the aerosol decomposition. Typical collection rates of the powders were about 1 g/h. Exposure of the powder on the filter to water or high humidity must be avoided. To prevent condensation and to reduce the relative humidity during powder collection, the filter was heated to 60-70 °C. The powders were unloaded from the filter inside a dry box. The precursor powders were then post-annealed in 0.1 atm of oxygen at 700 °C for 4 h to reduce the level of carbon present. Annealing in high purity oxygen gas was found to be crucial. The precursor powders were then mixed with Tl_2O_3 with the typical composition of Tl_x; x = 0.6-1.0, sealed in a gold tube and heat-treated in flowing oxygen between 650-890 °C for various reaction times. The details of the starting nominal compositions, reaction temperatures, and reaction times are reported in Table I.

TABLE I
SUMMARY OF VARIOUS Tl-PHASES OBTAINED FROM Ba-Ca-Cu-Ag-O BASED AEROSOL PRECURSOR POWDERS

S. No.	Starting Nominal Compositions[a]	Reaction Temp. (°C)	Reaction Time (h)	XRD Results[b]
1.	$Tl_{1.00}Ba_{1.05}Ca_{2.02}Cu_{3.00}Ag_{0.32}O_y$	650-775	12	Tl-2212
		800-830	6	Tl-2212
		850-880	3	Tl-2223
		890	0.50	Tl-2223
2.	$Tl_{0.80}Ba_{1.05}Ca_{2.02}Cu_{3.00}Ag_{0.32}O_y$	850	0.50	Tl-2223
3.	$Tl_{0.60}Ba_{1.05}Ca_{2.02}Cu_{3.00}Ag_{0.32}O_y$	840	0.33	Tl-1223;Tl-2223
4.	$Tl_{1.00}Ba_{1.92}Ca_{2.10}Cu_{3.00}Ag_{0.36}O_y$	650	2	Tl-1212;Tl-2212
		750-830	1	Tl-2212
		850-880	1	Tl-2223
5.	$Tl_{0.80}Ba_{1.92}Ca_{2.10}Cu_{3.00}Ag_{0.36}O_y$	850	1	Tl-2223
6.	$Tl_{0.80}Ba_{2.00}Ca_{2.00}Cu_{3.00}Ag_{0.40}O_y$	650-700	1	Tl-1223;Tl-1212
		750-800	1	Tl-2212
		830-865	1	Tl-2223

[a]some of the compositions were determined from ICP analysis.
[b]only major phases are reported

The samples were characterized by X-ray powder diffraction (XRD). Carbon content was determined by the LECO Carbon analyzer and chemical compositions were determined by ICP. Grain morphology and grain size were obtained using scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

The room-temperature X-ray powder pattern for the Tl-free precursor powders showed the presence of $BaCuO_2$, CaO, CuO and Ca-Cu-O phases. The SEM micrograph of the $Ba_2Ca_2Cu_3Ag_{0.37}O_7$ precursor powder is shown in Figure 2. The as-produced powders are homogeneous hollow spheres which are less than a micron in size. The carbon content for the as-produced aerosol precursor powders was of the order of 5000 ppm. After post-annealing at 700 °C in 0.1 atm oxygen for 4h, the carbon content was reduced to 2000 ppm.

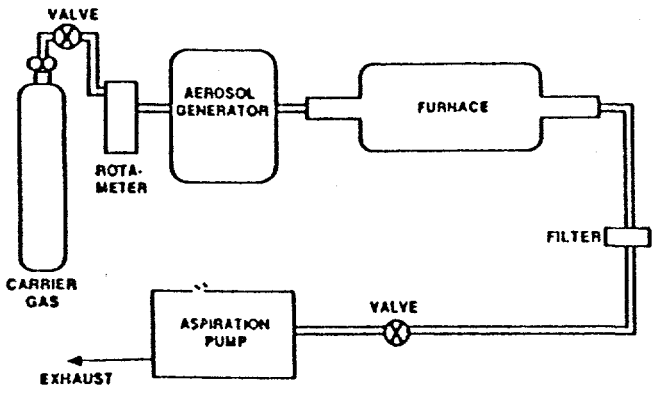

Fig. 1. Schematic diagram of the aerosol pyrolysis system.

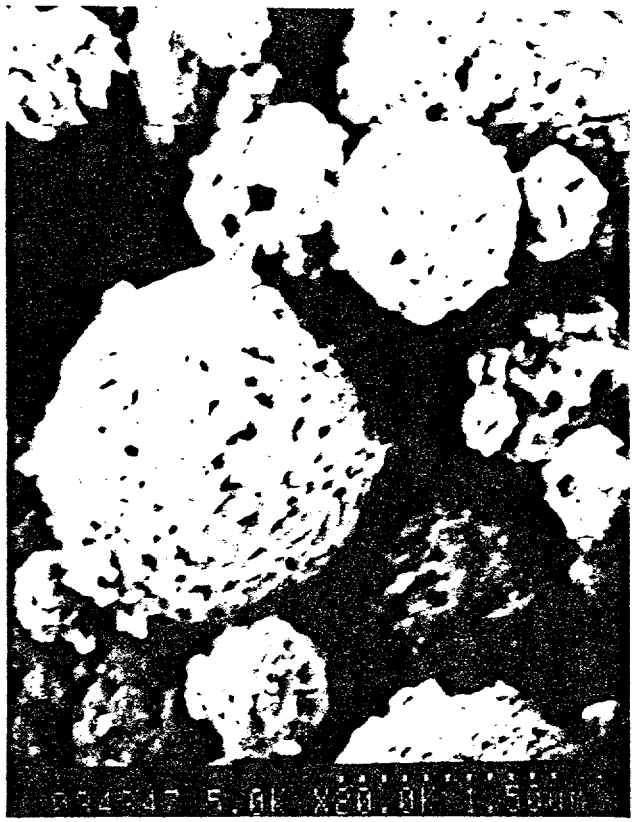

Fig. 2. Typical SEM micrograph of the as-produced aerosol precursor powders illustrating the presence of submicron size particles.

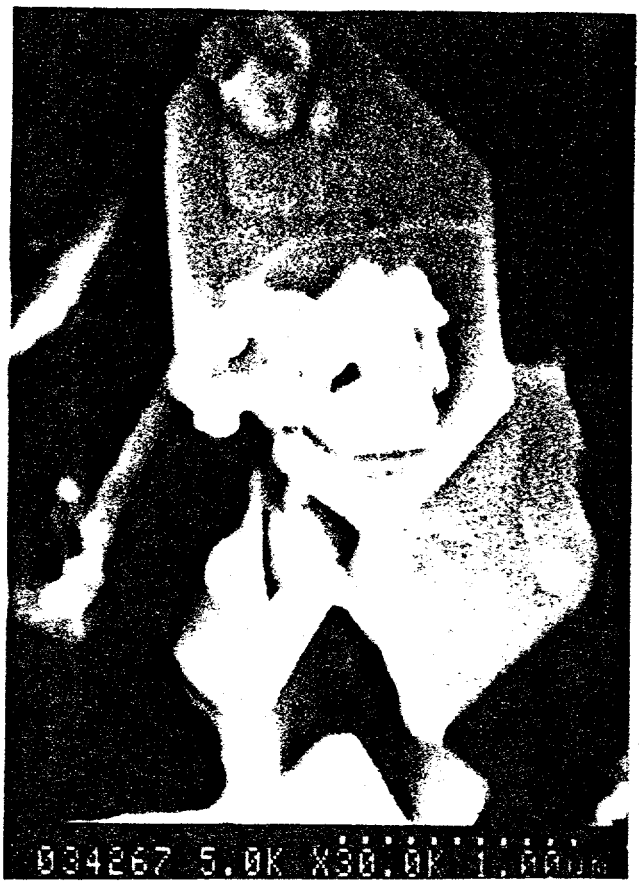

Fig. 3. SEM micrograph of the mixture of Tl-1212 and Tl-1223 superconductors.

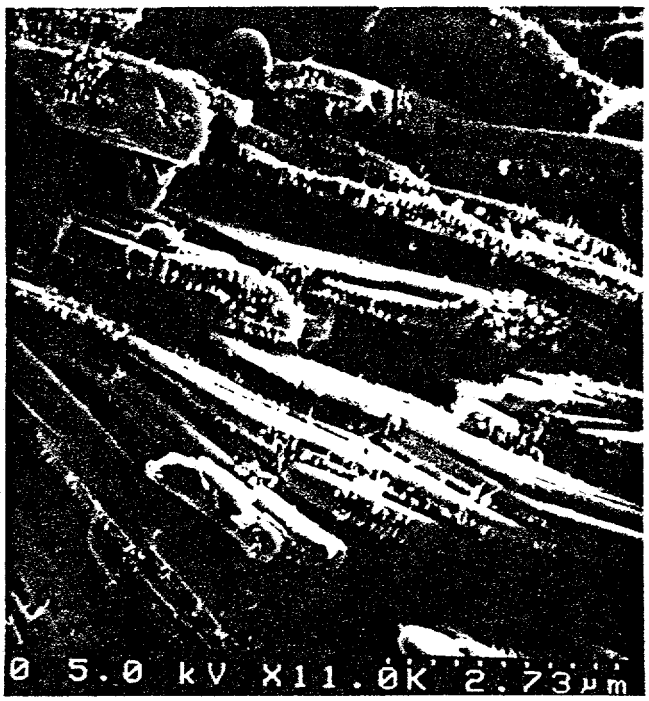

Fig. 4. SEM micrograph of the Tl-2212 superconductor.

The room-temperature XRD results for the heat-treated Tl-containing precursor powders are reported in Table I. In addition to the major phases reported, minor impurities such as $BaCuO_2$, CaO and CuO were also observed. In general, Tl-1212 and Tl-1223 phases formed below 700 °C while Tl-2212 formed between 700-830°C, and Tl-2223 formed above 830 °C. The SEM micrographs for the mixture of Tl-1212 and Tl-1223, Tl-2212, and Tl-2223, are shown in Figures 3, 4, and 5 respectively. These SEM micrographs clearly show the evidence for formation of highly anisotropic platelets. The Tl-2212 and Tl-2223 phases were stable over a wide range of temperatures.

We demonstrated the formation of various Tl phases from 1223 (or 1123) starting compositions at different processing temperatures. Efforts are being made to use these platelets for various conductor fabrication routes. Bayya et al. [6] also obtained highly anisotropic particles of Tl-2212 and Tl-2201 from the starting nominal compositions of 1223 by using NaCl-KCl as a molten salt medium at 850 °C with a reaction time of 1h.

ACKNOWLEDGMENT

M. P. thanks D. B. Beach for encouragement and Huey Hsu for helpful discussions.

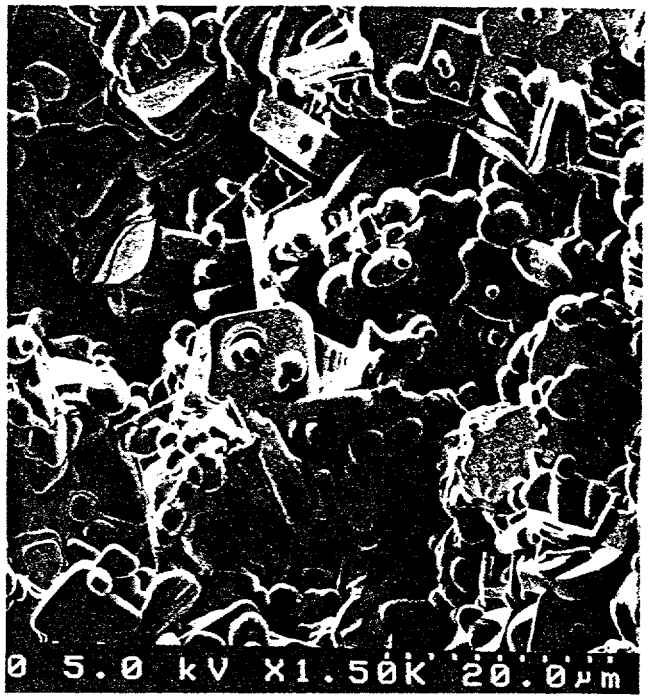

Fig. 5. SEM micrograph of the Tl-2223 superconductor illustrating the platelet formation.

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